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European Patent Office
Office européen des brevets



Publication number:

0 432 358 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **90114763.7**

(51) Int. Cl.⁵ **B01D 67/00, //B01D69:00**

(22) Date of filing: **01.08.90**

(30) Priority: **13.12.89 US 450691**
13.12.89 US 450705
13.12.89 US 450706

(43) Date of publication of application:
19.06.91 Bulletin 91/25

(84) Designated Contracting States:
BE DE DK ES FR GB IT NL

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(54) **Treated composite polyamide membranes to separate concentrated solute.**

(57) A reverse osmosis membrane having improved rejection of sulfuric acid and/or isopropanol is described. The membrane is prepared by treating a crosslinked, polyamide discriminating layer with a reagent that is amine-reactive or oxidizing such that the passage of sulfuric acid in a 2 percent aqueous solution at a transmembrane pressure of 400 psig (2758 kPa gauge) is reduced by at least 30 percent. The amine reactive reagent is a carboxylic acid ester, a carboxylic acid anhydride, an amine-reactive organic halogen compound, an ethylenically unsaturated hydrocarbon, or a 1,3-propane sultone. The oxidizing reagent is a peroxycarboxylic acid with a mw of less than 300, periodic acid, N-bromoamine or N-chloramine. A method of making the membrane and its use in separating a variety of solutes from water are also described.

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TREATED COMPOSITE POLYAMIDE MEMBRANES TO SEPARATE CONCENTRATED SOLUTE

This invention relates to treatment of composite polyamide membranes to enhance rejection of certain acids, bases, and organic materials and the use of such treated membranes in a reverse osmosis process.

Removal of materials dissolved or dispersed in a solution by separation of these materials from the dispersing medium or solvent utilizing reverse osmosis membranes is well known. The membranes used for reverse osmosis are selectively permeable to certain components of the mixture to be separated. Generally, water is the component to which such membranes are especially permeable. An aqueous feed solution is conveniently brought in contact with one surface of the reverse osmosis membrane under pressure so as to effect selective permeation of water through the membrane. This process is most generally used for desalination of water-containing salts. However, reverse osmosis has also been used to separate organic compounds and other materials from aqueous feed solutions.

The performance of reverse osmosis membranes has a critical effect on the efficiency and efficacy of reverse osmosis processes. Advantageously, the reverse osmosis membrane should be relatively impermeable to materials which are to be separated from the water and highly permeable to water. It has been found that membranes having a porous support which provides physical strength but imparts little or no rejection, combined with a thin discriminating layer adherent to the support, are particularly useful. Such membranes are commonly referred to as thin film composite membranes.

Polyamide membranes have been widely employed in reverse osmosis processes. U.S. Patent 4,277,344 describes a variety of membranes having a polyamide discriminating layer on a porous support. These membranes are preferably prepared by interfacial polymerization of a difunctional aromatic amine such as meta-phenylene diamine and a trifunctional aromatic acyl halide, such as trimesoyl chloride, optionally containing difunctional acyl halide. A 1,3,5-cyclohexane tricarboxyl chloride can also be employed as the acyl halide reactant. Such membranes are further illustrated in U.S. Patents 4,520,044 and 4,606,943. European Patent Application Publication EP 0 211 633 also describes composite polyamide membranes.

The treatment of membranes to enhance performance is described in the prior art in a number of patents. U.S. Patent 3,551,331 describes a process for modifying the permeability of a substantially linear aliphatic polyamide membrane. In this process, the polyamide membrane is treated with a protonic acid, lyotropic salt or a Lewis acid.

U.S. Patent 3,877,978 describes use of copolymers of vinyl acetate with various ethylenically unsaturated carboxylic acids to enhance the rejection of certain semi-permeable membranes.

U.S. Patent 3,886,066 discloses the use of hydrolyzable tannins to reduce the salt passage through semi-permeable membranes.

U.S. Patent 4,214,020 describes a process for coating exteriors of hollow fiber membranes to enhance their membrane characteristics.

U.S. Patent 4,634,531 describes the use of sequential treatment with a water-soluble amine and a water-soluble aldehyde to improve selective permeation.

U.S. Patent 4,704,324 teaches preparation of membranes by reaction of a nucleophilic first compound with a second compound bearing reactive onium groups.

U.S. Patent 4,812,238 describes the treatment of composite polyamide membranes with nitrous acid or a diazonium compound. The nitrous acid is disclosed to react with pendant amine groups.

U.S. Patent 4,828,700 discloses that reverse osmosis membranes can be treated with polymers bearing carboxylic acid groups and optionally pendant hydroxyl or amide moieties to enhance salt rejection.

U.S. Patent 3,904,519 describes treatment of linear aromatic polyamides with certain crosslinking reagents to improve flux or flux stability of the resulting membranes. Crosslinking reagents employed include aldehydes, polyamines, polycarboxylic acids, polyisocyanates, oxidizing agents, peroxides and other compounds.

U.S. Patent 3,951,815 describes a composite semi-permeable membrane formed of an ultrathin film of polyethylenimine on a support, where said film has been crosslinked with difunctional or trifunctional acyl halides, chloroformates, isocyanates and sulfonyl chlorides.

Existing commercial composite polyamide membranes display a good combination of high water flux, good salt rejection and acceptable chemical stability. Membranes which are more tolerant of acidic or basic conditions and which demonstrate a higher rejection for organic materials while maintaining high water flux are still sought.

The invention is, in one embodiment, a treated composite, crosslinked polyamide reverse osmosis membrane, prepared by a process comprising contacting a composite membrane having a crosslinked polyamide discriminating layer with a solution of an effective amount of reagent that is amine-reactive or a

compatible oxidant, whereby passage through the membrane of a selected solute in an aqueous solution of a given concentration at 25° C and equivalent operating pressure is reduced by at least 30 percent, more preferably 50 percent, relative to the membrane prior to treatment and the water flux of said membrane is reduced by not more than 50 percent, preferably not more than 40 percent, after treatment. Selected

solutes include sulfuric acid, sodium hydroxide, isopropanol or sodium nitrate.

It has been found that this process employing treated membranes results in a higher rejection than the membrane prior to treatment with minimum loss of flux in separation of purified water from aqueous streams containing the selected solute.

Another aspect of the invention is an improved process for separating water from an aqueous solution containing at least one selected solute, for which the solute passage through a membrane is at least twice that of sodium chloride at like conditions. By "like conditions" is meant equivalent transmembrane pressure, solute concentration and temperature. This process comprises (a) contacting a first side of a treated composite crosslinked polyamide membrane described above with an aqueous feed solution containing said selected solute, at conditions where a chemical potential exists between the first side and a second side of the membrane, whereby water having a reduced concentration of the selected solute diffuses through the membrane from the first to second side; and (b) collecting the purified water.

Composite reverse osmosis membranes having crosslinked polyamide discriminating layers are advantageously derived from reactants, comprising: (a) a compound or polymer bearing at least two primary amine groups and (b) a compound or polymer bearing an average of more than two carboxylic acyl halide groups. The amine and acid halide reactants may be aliphatic, cycloaliphatic or aromatic. Aromatic amines, compounds wherein one or more amine groups are bonded to a carbon atom in an aromatic ring, are especially preferred. The amine compound may contain one or two fused or separate aromatic rings in preferred embodiments.

The carboxylic acid halide reactant employed to prepare the polyamide discriminating layer desirably includes an aromatic acyl halide bearing at least three acyl halide groups. The carboxylic acid halide reactant may comprise some compounds or polymers which are difunctional. Preferably, at least 50 mole percent of the carboxylic acid halide reactant is trifunctional or more highly functionalized. The compound bearing the two acyl halide groups optionally bears other substituents that do not interfere with the reaction forming the membrane. Preferably, the carboxylic acid halide is trimesoyl halide. Advantageously, the carboxylic acid halide reactant is trimesoyl halide or cyclohexane-1,3,5-tricarbonyl halide or mixtures of these trifunctional halides. Optionally, isophthaloyl halide and/or terephthaloyl halide may be employed with one or both of the trifunctional halides. The halide is preferably chloride, but may be bromide.

The aromatic amine compound optionally may bear other substituents which do not interfere with the membrane formation reaction. For example, a compound bearing two primary amine groups and one group which has a carbonyl function not adjacent to the amine group, as described in U.S. Patent 4,761,234, may be employed but is not preferred. The preferred amine reactant employed to form the membrane is phenylene diamine, more preferably meta-phenylene diamine.

The composite crosslinked polyamide membrane can be prepared by techniques known in the prior art. Conveniently, interfacial polymerization of an aqueous amine applied to a microporous substrate with an acyl halide in an organic solution such as described in U.S. Patent 4,277,344, can be employed. Preferred as an organic solvent is an aliphatic hydrocarbon, such as hexane, or a chlorofluorocarbon, such as 1,1,2-trichlorotrifluoroethane. Other similar techniques for preparing such membranes are described in U.S. Patents 4,606,943; 4,520,044; 4,761,234; 4,772,394, and 4,828,700.

The microporous substrate on which these composite membranes are formed can be any substrate conveniently employed for this purpose. Suitable substrates for composite membranes have been extensively described in the prior art. Illustrative support materials include organic polymeric material such as polysulfone, polyether sulfone, chlorinated polyvinylchloride, styrene acrylonitrile copolymer, polybutylene terephthalate, cellulose esters and other polymers which can be prepared with a high degree of porosity and controlled pore size distribution. Porous inorganic material may also be operable as supports. Preferably, the surface pores in the support material will have a diameter 2000 Å or less, and the support material will have as high a porosity as is possible, while maintaining the desired pore size, integrity, and strength. Especially preferred as support layers are porous polysulfone films. These films are generally cast on non-woven fabric or woven cloth in the manner described in U.S. Patent 4,277,344. Surface active agents may be employed in the aqueous amine solution to enhance wetting of a hydrophobic substrate.

Especially preferred as membranes to be treated by the method described herein are the membranes disclosed in U.S. Patent 4,277,344. In preferred embodiments, these membranes are prepared by interfacial polymerization of meta-phenylene diamine and trimesoyl chloride. Such membranes are sold by FilmTec Corporation under the designation FT30 membranes.

In one embodiment of the invention, the membrane may be derived from amine reactants or acyl halide reactants which are polymeric. For example, a polymer made by reaction of a difunctional aromatic amine with trimellitic anhydride acid halide optionally mixed with trimesoyl halide, as described in U.S. Patent 4,606,943, is operable as the amine reactant, but is not preferred.

5 The polyamide of the membrane discriminating layer is crosslinked. These polyamides preferably have a crosslink density of at least 10 crosslinks, more preferably at least 50 crosslinks, per 100,000 molecular weight. The crosslink density can be determined by standard end-group analysis techniques and may be estimated by the insolubility or swelling of the resulting polyamide in solvents in which linear polyamides are soluble.

10 The rejection by the polyamide reverse osmosis membrane of specific solutes and the water flux of the membrane prior to treatment can operably vary over a wide range. The flux and rejection of specific solutes is determined with reference to test conditions using a specific concentration of solutes at a specific pressure and temperature. Preferably, the membrane to be treated will have a sodium chloride rejection of at least 90 percent, more preferably 95 percent, and a water flux of at least 12 gallons per square foot per
15 day [gfd] (488 L/m²·day), more preferably at least about 15 gfd (610 L/m²·day), when tested using an aqueous 0.2 weight percent sodium chloride solution at a transmembrane pressure of 200 lbs./sq. inch [psi] (1380 kPa) at 25°C. Membranes having a much higher flux and lower salt rejection prepared as described in U.S. Patent 4,765,897, can also be employed. Membranes having a higher salt rejection and useful with a
20 seawater feed at a pressure of 800 psi (5516 kPa) at 25°C with a flux of at least 10 gfd (407 L/m²·day) may also be treated.

The membrane may be in the form of a flat sheet, tubular or hollow fiber configuration. The membrane can be treated either prior to or after assembly into an element. In one especially preferred embodiment, the membrane is fabricated into a spiral membrane device and then treated by the method of this invention to produce a membrane element having enhanced rejection of sulfuric acid, sodium hydroxide and certain
25 organic compounds such as isopropanol.

It is found that the membranes to be treated by the method of this invention are desirably clean. In this context a "clean" membrane is a membrane which has not been subject to extensive service wherein the membrane flux or performance has been reduced by fouling. It has been found that membranes which are freshly prepared and have been subjected to only a brief test, (preferably less than 24 hours, more
30 preferably less than 1 hour) to determine initial reverse osmosis performance or no test prior to treatment are best suited to the treatments of this invention. Membranes which have been in service for an extended time and then are cleaned by standard techniques after being fouled are not as susceptible to treatment by the method of this invention.

Reactions of the selected reagents of the invention with the membrane may involve ring opening, as
35 well as oxidations, acylation or alkylation reactions. The present invention is not limited by any specific theory as to how the subject reagents enhance rejection of certain materials by the subject membranes. These different chemical modifications will not necessarily affect rejection of all solutes in the same manner. Rejection of some solutes may be enhanced after treatment while rejection of other solutes may decrease. The amine-reactive reagents employed herein are believed to react with pendant amine groups remaining in
40 the desalinizing layer to cap or crosslink such groups. A similar reaction was postulated for treatment for such membranes with nitrous acids in U.S. Patent 4,812,238. It is noteworthy that nitrous acid has been found to enhance sulfuric acid rejection of these membranes. The oxidizing reagents employed herein produce complex reactions which are not fully understood, but are believed to render amine groups less basic.

45 The reagent employed in treating the composite crosslinked polyamide membrane is reactive with hydrogens on primary or secondary amines at the conditions employed for treatment or modifies the membrane via an oxidation reaction. This reaction may be a displacement reaction or an oxidation. Strong oxidizing reagents employed for an extended period of contact do not as conveniently provide the desired modification.

50 The reagent is preferably an amine-reactive organic halogen compound that will alkylate primary amine groups at conditions of treatment herein, a carboxylic acid anhydride, a carboxylic acid ester, a compatible oxidant, an amine-reactive ethylenically-unsaturated compound, nitrous acid, a precursor of nitrous acid or a 1,3-heterocyclic sultone. These reagents may be difunctional or more highly functional compounds in which case some additional crosslinking may be introduced into the desalinizing layer by the treatment. More
55 preferably, the reagents are monofunctional. The reagent may be inertly substituted, which means that the reagent may contain moieties in addition to the amine-reactive group, provided said moieties do not interfere with the desired reaction. Preferably, the amine-reactive reagent has a molecular weight of less than 300, more preferably less than 150.

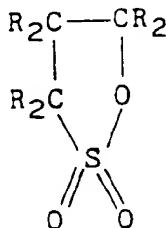
The alkylating, organic halogen reagents employed may include those activated by an electron withdrawing group, such as a carboxylic acid group, in the β position. The sodium salt of chloroacetic acid is especially preferred.

Illustrative carboxylic acid anhydride agents include acetic anhydride, and propionic anhydride, with acetic anhydride being especially preferred. Illustrative carboxylic acid ester reagents include methyl acetate and ethyl acetate, with methyl acetate being especially preferred.

The oxidizing reagents useful in the invention include a peroxycarboxylic acid, persulfuric acid or periodic acid, with peracetic acid being especially preferred. Strong oxidizing reagents, such as chromic acid, may deleteriously affect the membrane. The term "compatible oxidant" as used herein refers to oxidizing agents that do not deleteriously affect the properties of the composite membrane when employed for a short time period. Such oxidants preferably include peracetic acid and periodic acid. Sodium hypochlorite, the use of which for treatment of a reverse osmosis membrane is suggested in U.S. Patent 4,277,344 has now been found to not generally be a compatible oxidant, particularly if the solute is sodium hydroxide.

Ethylenically unsaturated compounds, such as acrylic acid or vinyl sulfonic acid, which react with primary or secondary amines, can also be employed. Some of these reagents, such as acrylic acid, are also zwitterion precursors at the appropriate pH. By the term "zwitterion precursor" is meant a compound which will react with a primary amine group to form a product containing both a positive and negative charge in the same molecule.

Illustrative of 1,3-heterocyclic sultone reagents are compounds corresponding to the formula:



where R at each occurrence is independently H or a C₁ to C₄ alkyl. Preferably, R at each occurrence is H, except one or two occurrences may be ethyl or methyl groups. R at each occurrence is most preferably H.

The reagent preferably contacts the discriminating layer of the composite crosslinked polyamide membrane while in a liquid diluent. Preferably, this diluent does not deleteriously affect either the discriminating layer or the support layer of the composite membrane. Advantageously, the amine reactive reagent is dissolved in the diluent. The suitability of a diluent will depend upon the specific composition of the desalinizing layer, the nature of the amine reactive agent and the composition of the support. An effective amount of the reagent is employed to impart the desired rejection properties to the membrane after treatment without deleterious effects on the membrane. An aqueous solution of 0.1 to 1 percent of the amine-reactive reagent or compatible oxidant is generally preferred. Diluents other than water may be preferred if water will react with the reagent. Co-solvents can be employed with water but are generally not necessary nor desirable. Suitable co-solvents include the lower alkanols, such as isopropanol or ethanol, and amides, such as N,N-dimethylformamide.

Amine-reactive reagents which react with or hydrolyze in water can be employed in other diluents. For example, acetic anhydride can be employed in an isopropanol diluent.

The time required for the desired properties to be imparted to the membrane will vary dependent on the nature of the desalinizing layer, the identity of the amine-reactive reagent or oxidizing reagent, temperature, concentration of the reagent, and other factors. Preferably, the reagent in water or other diluent should flow continuously over the membrane surface during treatment to replenish the reagent in contact with the surface. Typically, contact times in the range of 0.5 hour to 24 hours or more are desirable. The longer contact times are typically required with reagents of higher molecular weight, which will penetrate the desalinizing layer of the membrane slowly.

The temperature during treatment of the membrane is desirably maintained so as to avoid deleterious effects on the membrane. Too high a temperature may reduce flux through and or solute rejection by the membrane while too low a temperature may lead to undesirably long contact times for the treatment

Generally, temperatures in the range of 15° to 50° C, preferably 20° to 35°, are advantageous.

The treatment is conveniently conducted at atmospheric pressure, but a positive transmembrane pressure differential can optionally be employed.

The treatment of composite, crosslinked, polyamide reverse osmosis membranes described herein can enhance the rejection of specific compounds by such membranes. In particular, the rejection of sulfuric acid, sodium hydroxide, sodium nitrate and various organic compounds, such as isopropanol, can be affected by these treatments. Moreover, the rejection of common salts, such as sodium chloride, may also be enhanced by these treatments. Not all rejections of all compounds are necessarily affected to the same degree by various treatments. Sulfuric acid rejection can frequently be employed to indicate whether or not the treatment has in fact affected rejection of the membrane. Preferably, the aqueous feed solution has a pH in the range from about 1 to about 14, more preferably about 2 to about 13. However, it is desirable to evaluate any membrane with the particular stream with which said membrane will be employed in order to determine the effectiveness of this treatment in enhancing rejection of specific solutes.

The conditions employed for reverse osmosis for a specific feed can readily be determined by one skilled in the art. Transmembrane pressure must be great enough to overcome the osmotic pressure of the feed, but not so great as to cause excessive compaction, deleterious affects on the membrane element or excessive energy consumption in achieving the feed pressure. A transmembrane pressure of at least about 200 psi (1380 kPa) is employed with simple monovalent salts at concentrations up to about 0.1 molar concentration. Advantageously, the transmembrane pressure should be at least twice the osmotic pressure of the feed. The temperature during reverse osmosis must not adversely affect the membrane or its characteristics. A temperature in the range from zero to 50° C is generally convenient.

The following examples are presented to illustrate the invention, but are not otherwise intended to limit the subject invention. All parts and percentages are by weight unless otherwise indicated. Passage of a solute is in percent and is calculated by subtracting the rejection of said solute in percent from 100. Water flux is reported in gallons per square foot (of membrane) per day [gfd] and liters/square meter per day (L/m²·day). The concentration of the solute in the feed water is specified, as is the pressure of the feed during evaluation of the membrane performance. The temperature of the feed water during these reverse osmosis tests is ambient, generally about 18° to 25° C, and flux data was then normalized to 25° C using standard tables available for the commercial membrane of the type treated. The membrane used in the examples is a membrane available from FilmTec Corporation under the designation FT30 membrane, unless otherwise indicated.

The FT30 membrane is a composite crosslinked polyamide membrane having a polysulfone support and a desalinizing layer prepared by the interfacial polymerization of meta-phenylene diamine in an aqueous medium with trimesoyl chloride in an organic medium. The FT30 membrane is prepared in accordance with U.S. Patent 4,277,344. If the membrane is dried, it is desirable to employ a surface active agent prior to drying to make the membrane more readily wettable.

Example 1

Samples of FT30 membrane are evaluated in reverse osmosis tests employing four different aqueous solutions containing either 0.2 percent sodium chloride, 0.2 percent sodium nitrate, 0.2 percent sodium hydroxide, or 1000 parts per million isopropyl alcohol (IPA). Each of these four solutes is evaluated with a feed pressure of 200 pounds per square inch [psi] (1380 kPa). In addition, a solution of 2 percent sulfuric acid at a feed pressure of 450 psi (3103 kPa) is evaluated. The results of this evaluation are tabulated as Comparative Experiment 1 in Table I. The flux and rejection for each of the five feed streams is listed in the table.

A sample of FT30 membrane like that used in Comparative Experiment 1 is then treated with a 0.1 percent solution of acetic anhydride in isopropanol for a period of 24 hours at ambient temperature with no pressure applied across the membrane. The treated membrane is then retested with the five feed solutions employed with Comparative Experiment 1. The results of these evaluations are tabulated in Table I.

TABLE I

Membrane Treatment	0.2% NaCl at 200 psi (1380 kPa)		0.2% NaNO ₃ at 200 psi (1380 kPa)		2% H ₂ SO ₄ at 450 psi (3103 kPa)		0.2% NaOH at 200 psi (1380 kPa)		1000 ppm IPA at 200 psi (1380 kPa)	
	Flux (*)	Solute passage	Flux (*)	Solute passage	Flux (*)	Solute passage	Flux (*)	Solute passage	Flux (*)	Solute passage
Comparative Experiment 1	27 (1099)	2.6	27 (1099)	9.1	30 (1221)	7.2	23 (936)	20	30 (1221)	19
Example 1	21 (854)	2.4	21 (854)	7.3	21 (854)	1.9	16 (651)	15	22 (895)	15

(*) = L/m² day

It is apparent from Table I that the treatment with acetic anhydride decreased the flux of water through each membrane and also decreased the solute passage through said membrane. The decrease in solute passage for sodium chloride is minimal, but solute passage declines for the other solutes tested ranged from about 20 percent to over 70 percent. The flux declined by about 20 to 30 percent in each of the evaluations.

Example 2

A FT30 membrane is evaluated in sodium chloride rejection with a 0.2 percent aqueous solution at 200 psi (1380 kPa). The water flux through this membrane (Comparative Experiment 2) is 32 gfd (1302 L/m²·day) and solute passage was 3.6 percent. A FT30 membrane is then treated with a 0.1 percent solution of acetic anhydride in water with a transmembrane pressure of 200 psig (1380 kPa.g) for a period of 2 hours. The membrane after treatment exhibits a water flux of 22.3 gfd (907.4 L/m²·day) and a solute passage of 1.4 percent. This illustrates that treatment with acetic anhydride can be employed to raise the sodium chloride rejection of certain crosslinked polyamide composite membranes.

Examples 3 and 4

A FT30 membrane is tested for solute passage and flux with a 0.2 percent aqueous sodium chloride solution at 200 psi (1380 kPa), then a 1000 parts per million solution of isopropyl alcohol at 200 psi (1380 kPa) and then a 0.2 percent sodium nitrate solution at 200 psi (1380 kPa), followed by extended sodium chloride rejection testing for a period of over 450 hours. The results of these reverse osmosis tests are tabulated in Table II as Comparative Experiment 3.

A FT30 membrane like that in Comparative Experiment 3 is treated with acetic anhydride in a 0.1 percent solution in 90/10 water/isopropyl alcohol for a period of 24 hours at about 25° C. The resulting treated membrane is evaluated with feed streams in the same manner as the membrane in Comparative Experiment 3. The results of this evaluation are tabulated in Table II as Example 3.

In Example 4, a fresh clean sample of FT30 membrane is treated with 1,3-propane sultone in a 0.1 percent solution plus 0.1 percent Na₂CO₃ in 90/10 water/isopropyl alcohol at a temperature of about 25° C for 72 hours. The resulting membrane was also evaluated in reverse osmosis test in a manner similar to the membrane in Comparative Experiment 3 and results tabulated in Table II.

TABLE II

RO Test	Comparative Experiment 3		Example 3		Example 4	
	Flux. (L/m ² ·day)	Sol. Passage	Flux (L/m ² ·day)	Sol. Passage	Flux (L/m ² day)	Sol. Passage
0.2% NaCl at 200 psi initial	28 (1139)	5	19 (773)	1.4	22 (895)	0.9
1000 ppm IPA at 200 psi	30 (1221)	29	21 (854)	15	24 (977)	14
0.2% NaNO ₃ at 200 psi (initial)	29 (1180)	14.4	20 (814)	6	24 (977)	2.2
0.2% NaCl at 200 psi 48 hours	26 (1058)	3.6	24 (977)	3.5	24 (977)	0.9
0.2% NaCl 96 hours	25 (1017)	3.0	23 (936)	2.8	24 (977)	0.8
0.2% NaCl 120 hours	21 (854)	1.9	19 (773)	1.0	21 (854)	0.5

TABLE II (continued)

RO Test	Comparative Experiment 3		Example 3		Example 4	
	Flux (L/ m ² .day)	Sol. Passage	Flux (L/m ² .day)	Sol. Passage	Flux (L/m ² day)	Sol. Passage
0.2% NaCl 168 hours	18 (732)	1.2	16 (651)	1.0	18 (732)	0.4
0.2% NaCl 216 hours	16 (651)	1.0	16 (651)	0.9	17 (692)	0.4
0.2% NaCl 288 hours	16 (651)	0.8	16 (651)	0.8	17 (692)	0.4
0.2% NaCl 384 hours	14 (570)	0.9	14 (570)	1.0	15 (611)	0.4
0.2% NaCl 456 hours	16 (651)	1.0	16 (651)	1.0	17 (692)	0.5
0.2% NaCl after cleaning	19 (773)	1.2	17 (692)	1.2	20 (814)	0.7

Table II illustrates that treatment with acetic anhydride reduces the water flux of the treated membrane but more significantly reduces the solute passage of sodium chloride, isopropyl alcohol, and sodium nitrate through said membrane. In an extended test, the sodium chloride passage after 168 hours converges with that of the membrane in Comparative Experiment 3. In general, some decline in sodium chloride passage with time would be expected by one skilled in the art.

The treatment with 1,3-propane sultone decreases the flux less than the acetic anhydride treatment while reducing the solute passage to a greater degree. The passage of sodium chloride through the

membrane remains low throughout extended testing and the flux is comparable to that of Comparative Experiment 3.

Examples 5-8

5 A FT30 membrane similar to that employed in Comparative Experiment 1 is evaluated in Comparative Experiment 4 employing a 0.2 percent aqueous sodium chloride solution at 200 psi (1380 kPa), a sulfuric acid solution of pH 1 at 400 psi (2758 kPa) and a sodium hydroxide solution of pH 12 at 200 psi (1380 kPa), in three sequential reverse osmosis tests. A sample of membrane like that used in Comparative
10 Experiment 4 is treated with 0.2 percent acetic anhydride in a water solvent for 20 hours at about 25° C in Example 5. The treated membrane is then tested sequentially with sodium chloride, sulfuric acid, and sodium hydroxide feed streams like those used in Comparative Experiment 4 and the results are tabulated in Table III.

15 A sample of FT30 membrane is treated with 0.1 percent 1,3-propane sultone plus one percent NaHCO₃ in water at about 25° C for 20 hours and evaluated in the same reverse osmosis tests as Comparative Experiment 4. Results of these evaluations are tabulated in Table III as Example 6.

In Comparative Experiment 5, another sample of a commercially available crosslinked polyamide membrane sold under the designation of FT30 is evaluated in reverse osmosis tests using aqueous sodium chloride, sulfuric acid and sodium hydroxide like those employed for Comparative Experiment 4. The results
20 are tabulated in Table III.

A sample of the membrane like that employed in Comparative Experiment 5 is then treated with 1 percent aqueous peracetic acid for 24 hours at about 25° C. The resulting membrane was evaluated with reverse osmosis tests employing sodium chloride, sulfuric acid, and sodium hydroxide. The results of these evaluations are tabulated in Table III as Example 7.

25 In Example 8, a sample of the membrane like that employed in Comparative Experiment 5 is treated with a stirred 0.1 percent 1,3-propane sultone and one percent NaHCO₃ aqueous solution at about 25° C for 24 hours. The membrane is then evaluated using the same three feed streams as used in Comparative Experiment 5. The flux and solute passage of the treated membrane are tabulated in Table III.

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TABLE III

Comparative Experiment	Example	Treatment	RO Tests					
			0.28 NaCl at 200 psi (1380 kPa)		H ₂ SO ₄ (pH 1) at 400 psi (2758 kPa)		NaOH (pH 12) at 200 psi (1380 kPa)	
			Flux (*)	Solute Passage	Flux (*)	Solute Passage	Flux (*)	Solute Passage
4	--	Control	25 (1017)	3.1	18 (732)	24	28 (1139)	8.4
--	5	0.28 acetic anhydride	18 (732)	1.8	11 (448)	4.8	21 (854)	7.4
--	6	0.18 1,3-propane sultone	19 (773)	0.7	14 (570)	6.3	30 (1221)	2.9
5	--	Control	33 (1343)	4.3	33 (1343)	14	35 (1424)	15
--	7	18 Per-acetic acid	27 (1094)	1.2	20 (814)	1	25 (1017)	4.9
--	8	0.18 1,3-propane sultone	18 (732)	1.4	22 (895)	5.8	24 (977)	4.7
6	--	Lab formed FT30 control	14 (570)	0.8	24 (977)	7	21 (854)	4.0

(*) = (Liters/m²·day)

In Comparative Experiment 6, a membrane is formed by immersing by hand a polysulfone microporous support in aqueous meta-phenylene diamine and then treating said support with trimesoyl chloride in a 1,1,2-trichlorotrifluoroethane solvent at ambient temperature. The resulting laboratory-produced membrane was evaluated in reverse osmosis test as tabulated in Table III. It is interesting to note that the lab-prepared membrane without any treatment displays lower flux and lower solute passage than the commercially available membrane in Comparative Experiments 4 and 5. The treatments in Example 7 and 8 attain lower solute passages for sulfuric acid and sodium hydroxide than the membrane from which each is prepared. Likewise, the membranes of Examples 5 and 6 display lower flux and lower solute passages for both sulfuric acid and sodium hydroxide than the membrane of Comparative Experiment 4. The effects of these treatments on sodium chloride rejection are not as dramatic. The peracetic treatment appears to have the least affect on water flux. The peracetic acid significantly reduces solute passage of all the feed streams evaluated.

15 Examples 9-11

A control sample of a FT30 membrane is evaluated in Comparative Experiment 7 with three separate feed streams in a manner similar to Comparative Experiment 4. The three feed streams are 0.2 percent aqueous sodium chloride at 200 psi, sulfuric acid at pH 1 at 400 psi and sodium hydroxide at pH 12 at 200 psi.

In Comparative Experiment 8, a sample of the membrane like that evaluated in Comparative Experiment 7 is treated with 1 percent aqueous hydrogen peroxide at a pH of 7 for 20 hours at about 25°C. The treated membrane is then evaluated with the same three feed streams as Comparative Experiment 7 and the results of these evaluations are tabulated in Table IV.

A FT30 membrane is treated with 1 percent hydrogen peroxide plus 2 percent sulfuric acid in an aqueous solution at about 25°C for 20 hours. The treated membrane is then evaluated with aqueous feed streams of various solutes and their results are tabulated in Table IV as Comparative Experiment 9.

In Comparative Experiment 10, a sample of FT30 membrane is treated with an aqueous solution of 1 percent hydrogen peroxide and 1 percent acetic acid for 20 hours at about 25°C. The treated membrane is then evaluated in reverse osmosis tests and the results of these tests are tabulated in Table IV.

In Comparative Experiment 11, another sample of an FT30 composite polyamide membrane is evaluated in reverse osmosis tests using three solutes as tabulated in Table IV. A sample of FT30 membrane is treated with an aqueous solution of 1 percent hydrogen peroxide and 0.1 percent sodium hydroxide at a pH of 9 for a period of 20 hours at about 25°C. The treated membrane is evaluated in reverse osmosis tests and results are reported in Table IV as Comparative Experiment 12.

A sample of the membrane like that evaluated in Comparative Experiment 11 is treated for 1 hour at about 25°C with an aqueous solution of 1 percent peracetic acid, at a pH of 1.5. The resulting treated membrane was evaluated in reverse osmosis tests and the results of these tests are shown in Table 4 as Example 9.

A sample of the membrane like that evaluated in Comparative Experiment 11 is treated with an aqueous solution of 1 percent peracetic acid for 24 hours at about 25°C. This membrane is evaluated in reverse osmosis tests and the results of these tests are reported in Table 4 as Example 10.

In Comparative Experiment 13 another sample of commercially available membrane sold under the designation FT30 membrane by FilmTec Corporation is evaluated in reverse osmosis test and the results of these tests are shown in Table IV. A sample of FT30 membrane employed is then treated with 100 parts per million of sodium hypochlorite for 24 hours at about 25°C. The treated membrane is then evaluated in a series of reverse osmosis tests and results of these test are tabulated in Table IV as Example 11

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TABLE IV

Comparative Experiment	Example	Treatment	RO Tests					
			0.2% NaCl at 200 psi (1380 kPa)		H ₂ SO ₄ at 400 psi (2758 kPa)		NaOH at 200 psi (1380 kPa)	
			Flux (*)	Sol. Passage	Flux (*)	Sol. Passage	Flux (*)	Sol. Passage
7	--	Control	29 (1180)	4.9	34 (1383)	16	28 (1139)	27
8	--	1% H ₂ O ₂ (neutral pH)	25 (1017)	4.4	33 (1343)	12	28 (1139)	24
9	--	1% H ₂ O ₂ + 2% H ₂ SO ₄	28 (1139)	5.6	33 (1343)	17	27 (1099)	29
10	--	1% H ₂ O ₂ + 1% acetic acid	30 (1221)	6	32 (1302)	16	27 (1099)	27
11	--	Control	28 (1139)	7.3	32 (1302)	9.7	32 (1302)	9.7
12	--	1% H ₂ O ₂ + 0.1% NaOH (pH 9)	32 (1302)	4.4	36 (1465)	18	36 (1465)	11
--	9	1% peracetic acid (pH 1.5) (1 hour)	24 (977)	5.0	23 (936)	3.7	25 (1017)	6.3
--	10	1% peracetic acid (24 hour)	23 (936)	2.8	22 (895)	2.1	24 (977)	4.6
13	--	Control	21 (804)	9.3	27 (1099)	18	24 (977)	21
--	11	100 ppm NaOCl, 14 hours	27 (1099)	3.4	25 (1017)	1.2	62 (2523)	45

(*) = (L/m²·day)

From the data in Table IV it is apparent that peracetic acid significantly increased the rejection of the membrane for all solutes evaluated with little impact on the flux of said membrane. The membrane samples treated with hydrogen peroxide at various pH's showed much less decrease in solute passage but also little affect on the water flux was observed.

The membrane treated with sodium hypochlorite showed enhanced water flux and sodium chloride

rejection as is taught in U.S. Patent 4,277,344. The sulfuric acid rejection of the membrane was increased with minimal decrease in flux. However, the sodium hypochlorite treatment in combination with sodium hydroxide testing results in a membrane with a very high flux and a very high solute passage

5 Examples 12-18

10 A control sample of a FT30 membrane was evaluated with two separate feed streams for reverse osmosis performance. The first stream contained 0.2 percent sodium chloride in an aqueous solution at a pressure of 200 psi (1380 kPa) and a second feed stream of 0.2 percent sodium nitrate at a feed pressure of 200 psi (1380 kPa). Two separate membranes were evaluated and the results are tabulated in Table V in Comparative Experiments 14 and 15.

In Example 12 a sample of FT30 membrane is treated with an aqueous 0.2 percent solution of 1,3-propane sultone for a period of 20 hours at about 25° C. The water flux and solute passage with the sodium chloride and sodium nitrate solutions are determined and the results are tabulated in Table V.

15 In Example 13 a 0.2 percent aqueous solution of the sodium salt methacrylic acid is used to treat a clean sample of FT30 membrane for a period of 20 hours. The water flux and solute passage with sodium chloride and sodium nitrate solutions are determined and are tabulated in Table V.

In Example 14 a sample of a clean membrane like that evaluated in Comparative Experiment 14 was treated with a 0.2 percent aqueous solution of the sodium salt of vinyl sulfonic acid for 20 hours. The treated membrane is then evaluated with sodium chloride and sodium nitrate and the results are tabulated in Table V.

Examples 12, 13 and 14 demonstrate that significantly reduced solute passages can be obtained by treatment with 1,3-propane sultone, the sodium salt of methacrylic acid and the sodium salt of vinyl sulfonic acid with only minimal, if any, decrease in water flux.

25 In Examples 15, 16, 17, and 18 samples of clean membrane like that evaluated in Comparative Experiment 15 were treated with various aqueous solutions of reagents as listed in Table V. All these reagents are at concentrations of 0.2 percent in the aqueous solution and the treatment time is 20 hours. The untreated membrane in Comparative Experiment 15 possesses a higher sodium chloride passage than the membrane in Comparative Experiment 14. A greater decrease in flux after treatment with reagents is
30 observed in Examples 15-18 than is observed in Examples 12-14.

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TABLE V

Comparative Experiment	Example	Membrane Treatment	RO Tests Results			
			0.2% NaCl at 200 psi (1380 kPa)		0.2% NaNO ₃ at 200 psi (1380 kPa)	
			Flux **	Solute Passage	Flux **	Solute Passage
14	--	Control	24 (977)	2	25 (1017)	5.6
--	12	1,3-Propane Sultone	20 (814)	0.4	22 (895)	1.1
--	13	Methacrylic Acid*	27 (1099)	1.0	29 (1180)	4
--	14	Vinyl Sulfonic Acid*	27 (1099)	1.0	29 (1180)	4.6
15	--	Control	34 (1383)	5.0	37 (1505)	12
--	15	Methacrylic Acid*	19 (773)	2.1	22 (895)	5.3
--	16	Vinyl Sulfonic Acid*	20 (814)	1.7	23 (936)	4.3
--	17	Acrylamide	20 (814)	2.2	24 (977)	5.7
--	18	Chloroacetic Acid	21 (854)	1.6	26 (1058)	5

*In the sodium salt form.

** (L/m²·day)Examples 19 and 20

A commercially available FT30 membrane is coated with an aqueous solution of 42.5 percent phosphoric acid, the excess acid is then allowed to drain from the surface and the treated membrane dried at a 120°C until the surface appears visibly dry. This treatment is generally as described in Example 4 of U.S. Patent 4,765,897. The resulting membrane, as indicated in Table VI as Comparative Experiment 16, possesses a flux of 33 gfd (1343 L/m²·day) and solute passage of 70 percent using a 0.2 percent aqueous

sodium chloride solution at 100 psi (690 kPa).

A clean sample of FT30 membrane is then treated with a 0.1 percent aqueous solution of 1,3-propane sultone for a period of 20 hours. The resulting treated membrane was tested once again with 0.2 percent sodium chloride at 100 psi and the results are tabulated as Example 19 in Table VI. The solute passage was reduced by more than two-thirds and the flux actually increased.

The membrane treated with 1,3-propane sultone was then treated with a colloid of tannic acid in a general manner described in Example 12 of U.S. Patent 4,765,897. The resulting membrane was tested using a 0.2 percent sodium chloride solution at 100 psi. The results are tabulated in Table VI as Example 20.

TABLE VI

Comparative Experiment	Example	Treatment	0.2% NaCl 100 psi	
			Flux gfd (L/m ² day)	Solute Passage (%)
16	--	FT30 coated 42.5% H ₃ PO ₄ Heated at 120°C	33 (1343)	70
--	19	0.1 % 1,3-propane sultone	39 (1587)	22
--	20	Example 19 treated with tannic acid	14 (570)	6

Examples 21-23

Two samples of a commercial FT30 membrane are tested to determine the water-flux and solute passage with four different feed streams in Comparative Experiment 17. The feed streams include 0.2 percent sodium chloride, 0.2 percent sodium nitrate, sulfuric acid at a pH of 1 and sodium hydroxide at a pH of 12. All tests, except the sulfuric acid, are conducted at 200 psi (1380 kPa). The sulfuric acid test is conducted at 400 psi (2758 kPa). Samples of membrane like those evaluated in Comparative Experiment 17 are treated with 0.1 percent aqueous peracetic acid in Example 21, with 0.1 percent periodic acid in Example 22 and with 1,000 parts per million chloramine in Example 23. All the treatment solutions are aqueous solutions and the treatments are for a period of three days at a temperature in the range of about 25°C.

The treated membranes are then evaluated in reverse osmosis tests and the results are tabulated in Table VII.

TABLE VII

Comparative Experiment	Example	Treatment	RO Tests							
			0.2% NaCl at 200 psi (1380 kPa)		0.2% NaNO ₃ at 200 psi (1380 kPa)		H ₂ SO ₄ , pH 1 at 400 psi (2758 kPa)		NaOH, pH 12 at 200 psi (1380 kPa)	
			Flux (*)	Solute Passage	Flux (*)	Solute Passage	Flux (*)	Solute Passage	Flux (*)	Solute Passage
17	--	Control	17 (692)	12.3	21 (854)	16.1	21 (854)	13.5	18 (732)	17
			16 (651)	8.2	20 (814)	7.2	20 (814)	13.8	17 (692)	16
--	21	0.1% Peracetic Acid	14 (570)	4.2	18 (732)	7.4	19 (773)	1.9	17 (692)	8
			15 (610)	4.6	19 (773)	8.2	20 (814)	2.2	18 (732)	8
	22	0.1% Periodic Acid	33 (1343)	5.4	34 (1383)	10.1	43 (1750)	2.9	53 (2157)	23
			33 (1343)	5.1	34 (1383)	10.6	42 (1709)	2.5	53 (2157)	23
	23	1000 ppm Chloramine	34 (1383)	10.1	36 (1645)	11.5	43 (1750)	5.4	40 (1628)	13
			34 (1383)	10.6	--	15.1	42 (1709)	6.8	39 (1587)	14

* = L/m²·day

The peracetic acid treated membranes generally show the lowest solute passage with all of the solutes after treatment. The periodic acid treatment shows generally higher fluxes than the membrane prior to treatment and reduced solute passage for sulfuric acid and sodium chloride. The solute passage of sodium nitrate after the periodic acid treatment was lower than the FT30 control membrane but higher than the peracetic acid-treated membrane. The periodic acid treated membrane showed very high flux and poor solute passage in testing with sodium hydroxide. The chloramine-treated membrane also showed higher fluxes than the control, but the solute passages were generally comparable after chloramine treatment to that of the membrane prior to the treatment with the exception of the sulfuric acid solute passage which was reduced by more than 50 percent.

Examples 24-26

In Comparative Experiment 18 a FT30 membrane is evaluated in reverse osmosis tests with four solutions in a manner similar to Comparative Experiment 17. Two samples of FT30 membrane are then treated with either peracetic acid, periodic acid, or chloramine in the general manner of Examples 21, 22 or 23, respectively, except that the treatment was 24 hours in duration. The results of the reverse osmosis tests of the control and treated membranes are tabulated in Table VIII.

TABLE VIII

Comp. Exp.	Example	Membrane Treatment	RO Tests											
			0.2% NaCl at 200 psi (1380 kPa)		0.2% NaNO ₃ at 200 psi (1380 kPa)		1000 ppm IPA at 200 psi (1380 kPa)		H ₂ SO ₄ , pH 1 at 400 psi (2758 kPa)		NaOH, pH 12 at 200 psi (1380 kPa)			
			Flux (*)	Solute Passage	Flux (*)	Solute Passage	Flux (*)	Solute Passage	Flux (*)	Solute Passage	Flux (*)	Solute Passage		
18	--	Control	33 (1343)	2.5	36 (1465)	14.8	39 (1587)	19	36 (1465)	8.4	32 (1302)	8.8		
			34 (1383)	2.6	38 (1546)	15.4	41 (1668)	19	26 (1058)	8.4	33 (1343)	9.0		
--	24	0.1% Peracetic Acid	24 (977)	1.3	27 (1099)	6.8	30 (1221)	16	26 (1058)	0.8	22 (895)	5.6		
			24 (977)	1.2	26 (1058)	5.1	28 (1139)	16	25 (1017)	0.7	21 (854)	5.4		
--	25	0.1% Periodic Acid	21 (854)	2.6	23 (936)	10.9	28 (1139)	22	23 (936)	5.2	19 (773)	7.4		
			22 (895)	4.1	25 (1017)	14.7	25 (1017)	26	23 (936)	6.3	20 (814)	8.6		
--	26	1000 ppm Chloramine	24 (977)	1.7	26 (1058)	5.5	26 (1058)	27	25 (1017)	1.6	26 (1058)	8.4		
			24 (977)	2.3	27 (1099)	7.2	28 (1139)	28	26 (1058)	1.8	27 (1099)	8.7		

* = L/m²·day

The water flux of all the membranes is somewhat reduced by the treatments but the solute passage is likewise reduced with the exception of the membranes treated with periodic acid and chloramine, which show increased solute passage for isopropyl alcohol.

Examples 27-30

A composite crosslinked polyamide membrane intended for use in seawater desalination and available commercially under the designation SW30HR from FilmTec Corporation is evaluated with simulated seawater containing 3.5 percent mixture of sodium chloride and other salts at 800 psi (5516 kPa). The SW30HR membrane is similar in composition to the FT30 membrane. The composition of the simulated seawater is:

	Percent by Weight
NaCl	58.49
MgCl ₂ ·6H ₂ O	26.46
NaSO ₄	9.75
CaCl ₂	2.765
KCl	1.645
NaHCO ₃	0.477
KBr	0.238
H ₃ BO ₃	0.071
SrCl ₂ ·6H ₂ O	0.095
NaF	0.007

The flux and solute passage of two samples of this membrane are tabulated in Table IX as Comparative Experiment 19.

Samples of the SW30HR control are then treated with 0.1 percent aqueous peracetic acid for 24 hours in Example 27. The flux and solute passage of the treated membrane with simulated seawater is tabulated in Table IX.

The SW30HR membrane in two samples is treated with 0.1 percent periodic acid for 25 hours. The reverse osmosis test results for these samples are tabulated in Table IX as Example 28.

TABLE IX

Comparative Experiment	Example	Treatment	RO Tests	
			3.5% SSW at 800 psi (5516 kPa)	
			Flux (L/m ² day)	Solute Passage
19	--	SW30HR Control	13 (529)	0.5
"			14 (570)	0.5
--	27	0.1% Peracetic Acid, 24 hrs.	11 (448)	0.4
	"		11 (448)	0.4
--	28	0.1% Periodic acid, 25 hrs.	15 (610)	1.4
	"		15 (610)	1.6
--	29	1000 ppm Chloramine	25 (1017)	1.0
	"		24.2 (985)	1.7
--	30	1000 ppm Chloramine adjusted to pH 1	11 (448)	0.6
	"		10 (407)	0.6

Two samples of the SW30HR membrane are treated with 1000 parts per million chloramine in water for 20 hours. The reverse osmosis tests in Example 29 results indicated a higher water flux and moderately higher solute passage.

In Example 30, the SW30HR membrane was also treated with 1000 parts per million chloramine but in a solution adjusted to a pH of 1. The water flux of this treated membrane was slightly lower than prior to treatment and the solute passage was marginally increased.

Example 31

A commercially available FT30 membrane is coated with 85 percent phosphoric acid and treated at 120°C as generally described in U.S. Patent 4,765,897. It is then incorporated into spiral wound reverse osmosis elements.

A clean sample of this membrane in spiral element form is treated with 0.3 percent peracetic acid for 16 hours. The resulting membrane element along with an untreated control, is then treated with a tannic acid colloid as described in U.S. Patent 4,765,897. Both membranes were subjected to the following series of tests: (1) tested on 0.2 percent MgSO₄ at 70 psi (483 kPa), (2) stored in a biostatic storage solution for 15 days, (3) retested on 0.2 percent MgSO₄ at 70 psi (483 kPa), and (4) tested on 0.2 percent H₂SO₄ at 70 psi (483 kPa). Results appear in Table X.

TABLE X

	Treatment	0.2 Percent MgSO_4 at 70 psi (483 kPa)		0.2 percent MgSO_4 Retest** at 70 psi (483 kPa)		0.2 percent H_2SO_4 at 70 psi (483 kPa)	
		Flux gpd (*)	Percent Rejection	Flux gpd (*)	Percent Rejection	Flux gpd (*)	Percent Rejection
Comparative Experiment 20	Control	330 (13427)	98.8	281 (11434)	98.1	296 (12044)	25.9
Example 31	0.3% peracetic acid for 16 hours followed by tannic acid colloid	262 (10660)	99.1	228 (9277)	98.4	241 (9806)	93.2

(*) = $\text{L/m}^2\text{-day}$

** After storage for 15 days in biostatic solution consisting of 1.0 percent by weight sodium metabisulfite dissolved in 80:20 water:propylene glycol.

Claims

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1. A composite crosslinked polyamide membrane for reverse osmosis, comprising:
a crosslinked polyamide discriminating layer treated with a reagent that is amine-reactive or oxidizing such that said membrane after treatment, relative to the membrane prior to treatment, has a water flux of at least 50 percent and passage of H₂SO₄ in a 2 percent aqueous solution at 400
10 psig (2758 kPa gauge) and 25° C is reduced by at least 30 percent.
2. The membrane of Claim 1 wherein the polyamide discriminating layer is derived from reactants comprising (a) a compound or polymer bearing at least two primary amine groups and (b) a compound or polymer bearing an average of more than two carboxylic acid halide groups.
- 15 3. The membrane of Claim 2 wherein (b) is a trimesoyl halide, cyclohexane-1,3,5-tricarbonyl halide, mixtures thereof or mixtures of either with isophthaloyl halide or terephthaloyl halide.
4. The membrane of Claim 2 wherein (a) comprises at least 50 mole percent m-phenylenediamine, (b) comprises at least 50 mole percent trimesoyl halide and the polyamide discriminating layer is formed
20 by interfacial polymerization of (a) and (b) on a microporous substrate.
5. The membrane as described in Claim 4 wherein (a) consists essentially of m-phenylenediamine, (b) consists essentially of trimesoyl chloride, the substrate is made from polysulfone and the membrane to be treated is clean.
- 25 6. The membrane of Claim 1 wherein the oxidizing reagent is a peroxycarboxylic acid with a molecular weight of less than 300, periodic acid, N-bromoamine or N-chloramine.
- 30 7. The membrane of Claim 1 wherein the amine reactive reagent is an organic halogen compound that reacts with a primary or secondary amine by means of an alkylation reaction, a carboxylic acid anhydride, a carboxylic acid ester, a 1,3-heterocyclic sultone having 3 carbon atoms in the ring or an amine-reactive ethylenically unsaturated compound.
- 35 8. The membrane of Claim 7 wherein the membrane is contacted with 1,3-propane sultone, acetic anhydride, methacrylic acid, sodium methacrylate or sodium vinyl sulfonate.
9. A method of treating a composite crosslinked polyamide reverse osmosis membrane, to improve a solute rejection, comprising: contacting a composite membrane having a crosslinked polyamide discriminating layer with a solution of a reagent that is amine-reactive or oxidizing, such that passage
40 through the membrane of H₂SO₄ in a 2 percent aqueous solution at 400 psig (2758 kPa gauge) and 15° to 35° C is reduced by at least 30 percent relative to the membrane prior to treatment and water flux of said membrane is reduced by not more than 50 percent after treatment.
- 45 10. The method of Claim 9 wherein the polyamide discriminating layer is derived from reactants comprising (a) a compound or polymer bearing at least two primary amine groups and (b) a compound or polymer bearing an average of more than two carboxylic acyl halide groups.
11. The method of Claim 10 wherein reactant (a) is a phenylenediamine and (b) is trimesoyl halide, cyclohexane-1,3,5-tricarbonyl halide, mixtures thereof or mixtures of either with isophthaloyl halide or
50 terephthaloyl halide.
12. The method of Claim 10 wherein the polyamide discriminating layer is formed by interfacial polymerization of (a) and (b) on a microporous substrate.
- 55 13. The method as described in Claim 9 wherein said oxidizing reagent is a peroxycarboxylic acid of less than 300 molecular weight, periodic acid, N-chloramine or N-bromoamine.

14. The method of Claim 9 wherein said amine-reactive reagent is an organic halogen compound which reacts with a primary or secondary amine via an alkylation reaction, a carboxylic acid anhydride, a carboxylic acid ester, a 1,3-heterocyclic sulfone having 3 carbon atoms in the ring, or an amine-reactive ethylenically-unsaturated compound.

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15. The process of using a reverse osmosis membrane for separating water from an aqueous solution containing at least one selected solute which has a solute passage through a composite crosslinked polyamide membrane at least twice that of sodium chloride at like conditions, comprising:

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(A) contacting a first side of a treated composite crosslinked polyamide membrane with an aqueous feed solution containing said selected solute at conditions wherein a chemical potential exists between the first side and a second side of the membrane sufficient that water having a reduced concentration of the selected solute relative to the aqueous feed solution diffuses through the membrane from the first side to the second side; and

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(B) collecting the purified water from the second side of the membrane, wherein the treated composite, crosslinked polyamide membrane having properties of substantial tolerance to acidic or basic conditions and organic materials, while maintaining high water flux, is prepared by contacting:

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(i) a crosslinked polyamide discriminating layer derived from reactants comprising (a) a compound or polymer bearing at least two aromatic primary amine groups and (b) a compound or polymer bearing an average of more than two carboxylic acid halide groups, said reactants being interfacially polymerized on a microporous support, with

(ii) a reactant that is amine-reactive or oxidizing, such that the membrane, after treatment with said reagent, has relative to the untreated membrane, a water flux of at least 50 percent and passage of the selected solute is reduced by at least 30 percent.

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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 4763

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
A	EP-A-0 085 111 (TEIJIN LTD) * Page 24 * - - -		B 01 D 67.00 B 01 D 69.00		
A	WO-A-8 802 653 (BRUNSWICK CORP.) * Claims 16,17; pages 22-23 * - - -				
A,D	EP-A-0 275 027 (FILMTEC CORP.) - - -				
A	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 275 (C-516)[3122], 29th July 1988; & JP-A-63 54 905 (TORAY IND. INC.) 09-03-1988 - - - - -				
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
			B 01 D 67.00 B 01 D 69.00		
The present search report has been drawn up for all claims					
Place of search		Date of completion of search	Examiner		
The Hague		21 December 90	DEVISME F.R.		
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